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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Preservation of Documents for Storage

I, WILLIAM HERBERT LANGWELL, a British Subject, of 32, Copse Edge Avenue, Epsom, Surrey, England, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preservation of printed or written documents which are already old or which are required to be kept in storage for substantial periods of time.

Fibrous cellulosic webs such as paper remain in usable condition for a substantial but nevertheless limited period of time the extent of which depends largely upon the process by which the web has been produced and upon the conditions under which it is stored. The processes by which cellulosic webs have been produced have changed to a major degree over the last few centuries and there has also been change in the materials from which they are produced. There are now, however, substantial reasons for believing that cellulosic webs which are free from acid will have an almost indefinite life provided that they are kept reasonably dry and are protected from acid atmospheric pollutants such as sulphur dioxide.

Processes are already known for the preservation of documents. The most important of these rely upon lamination with plasticised cellulose acetate films for preserving and strengthening the documents. These processes have been the subject of an extensive investigation (see "Preservation of Documents by Lamination" by W. K. Wilson and B. W. Forshee, National Bureau of Standards Monograph No. 5). The conclusion is reached that in order to have a cellulose acetate film of maximum stability it should contain plasticisers that do not contribute to its degradation, an antioxidant and an acid acceptor. The acid acceptor has been considered necessary in order to remove sulphates which are present in even the purest grades of cellulose acetate, (sulphuric acid is used as a catalyst in acetylating cellulose): the removal of the sulphate removes an important potential source of degradation. The antioxidant is added because it has been shown that oxygen present in air will gradually degrade cellulose acetate unless steps are taken to prevent this. The recommended additions of both antioxidant and acid acceptor are 0.5% by weight of each based upon the overall weight of the cellulose acetate composition.

In addition it has been proposed to use a separate wet process for the deacidification of the document prior to lamination: this has involved neutralising the paper with consecutive washes with saturated solutions of calcium hydroxide and calcium bicarbonate. This prevents degradation of an applied layer of plasticised cellulose acetate but it is a difficult process to carry out particularly upon papers of low wet-strength. It is clearly an inconvenient step to operate in conjunction with a laminating operation.

Whilst it is true that cellulose acetate possesses most of the characteristics desirable for the preservation of documents it undoubtedly suffers from certain important disadvantages. Wilson and Forshee *loc.cit.* noted that papers already containing acid can be seriously degraded during lamination.

When using plasticised cellulose acetate (25% by weight of plasticiser) the documents to be preserved are exposed to temperatures of 170-180°C. for times of the order of 1 minute and then only cooled gradually. Preservation is particularly important for documents originating in the 18th Century and earlier and exposure to such temperatures for even a short time is sufficient, in the majority of cases, to induce a yellowing or browning (additional to any already present) which is not acceptable to librarians and archivists. The only alternative is the wet deacidification noted above and the various hazards involved are usually too great to

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warrant attempting the treatment.

It is accordingly an object of the present invention to place at the disposal of the archivist and librarian a process, and materials for use therein, which can safely be utilised for the preservation of documents originating in the 18th Century and earlier as well as for documents of more recent origin.

The present invention accordingly provides a process for the preservation of a document having as its basis an opaque fibrous cellulosic web which comprises applying to at least one surface of the said document a translucent thin colourless flexible web of organic fibrous material impregnated with a mixture of (a) substantially colourless flexible inert film-forming thermoplastic non-tacky material which is resistant to oxidation and degradation in air at room temperature and which will flow under pressure at temperatures not exceeding 120°C., and (b) at least one colourless acid-binding salt present in an amount at least sufficient to neutralise the acidity present in said opaque fibrous cellulosic web, the compacting of the resulting laminate under pressure at a temperature not exceeding 120°C. until said non-tacky material has adhered to the surface of said opaque fibrous cellulosic web. The invention also includes the impregnated organic fibrous material used in the above process.

It is most convenient for the archivist to be provided with a thin colourless material which can readily be cut to shape and used in a simple form of press which can be operated at temperatures not exceeding 120°C. Indeed for most purposes temperatures not exceeding 100°C. can be used and, if circumstances so require, the impregnated tissue may be formulated with a non-tacky polymer which will enable the process to be carried out at temperatures as low as 50°C. or even lower.

It is contemplated also that when a document is written or printed only upon one side the other side may be coated with a thicker strengthening tissue which need not necessarily satisfy all the requirements subsequently indicated for the coating layer applied to the side which is to be read. If preferred the second side can be given an entirely different treatment.

The impregnated thin colourless flexible web of organic fibrous material which is used in the present process is intended to act as a flexible reinforcing material. Such fibrous tissues *per se* will usually have a thickness of 1-2 mils when intended to be applied to the side of a document which is to be read but may be markedly thicker, e.g. 5-10 mils when intended for use as a strengthening tissue for application to the back of a document. The organic fibrous material may be a highly translucent tissue paper or a thin bonded-fibre fabric made from polyethylene terephthalate, from regenerated cellulose or from a superpolyamide such as polycaprolactam or polyhexamethylene adipamide. If the documents are to be exposed to light for substantial periods of time it is recommended not to use the superpolyamides but they are nevertheless very useful for application to the back of a document the other side of which will be mainly exposed. Bonded-fibre fabrics based upon polyethylene terephthalate are extremely useful in the present invention and provide reinforcing materials of outstanding strength, durability and ability to undergo repeated flexing.

The substantially colourless inert film-forming thermoplastic non-tacky polymer with which the organic fibrous material is impregnated is a material which is flexible at room temperature in films having a thickness of 1 to 3 mils or which when plasticised with a suitable plasticiser is flexible under these conditions. The preferred compounds are polymers of monoethylenically unsaturated esters of monocarboxylic acids which polymers contain only carbon, hydrogen and oxygen atoms in the molecule. The lower alkyl ethers of cellulose when suitably plasticised may also be used.

The preferred polymers of monoethylenically unsaturated esters of monocarboxylic acids are polymers derived from monomeric esters containing four to eight, preferably four to six, carbon atoms in the molecule such as vinyl acetate, the alkyl acrylates having four to eight carbon atoms and the alkyl alkacrylates and crotonates having five to eight carbon atoms. Some of these esters can be used in the form of homopolymers, such as polyvinyl acetate, as well as in the form of interpolymers while other such esters can be used only in the form of copolymers as the tendency to form tacky films is far too pronounced—this applies particularly to methyl and ethyl acrylates. The alkyl alkacrylates used contain at least five carbon atoms, e.g. polymethyl ethacrylate, polymethyl *n*-butylacrylate and polyethyl methacrylate. Examples of copolymers which may be used include copolymers of one or more alkyl acrylates with one or more of the said alkyl alkacrylates, copolymers of vinyl acetate with one or more of the said alkyl acrylates and/or methacrylates and copolymers of vinyl acetate, or the said alkyl acrylates and/or alkacrylates with the lower dialkyl maleates. Other monomers, such as styrene and α-methylstyrene, which will not affect the resistance of the resulting polymers to oxidation and degradation may also be present in such copolymers so long as the proportion thereof does not substantially affect the film-forming ability and the flexibility of thin films of the resulting copolymers.

The preferred ether of cellulose is ethyl cellulose and this should be substantially plasticised. A saturated diester of phthalic

acid containing at least 4 carbon atoms in the molecule is suitable for this purpose, e.g. di-*n*-butyl or di(2-ethylhexyl) phthalate. Other plasticisers which can be used to produce a plasticised ethyl cellulose which flows below 120°C. under pressure may likewise be used: mixtures of such plasticisers may also be used. Any plasticisers used should not impair the resistance of the resulting plasticised composition to oxidation and degradation.

The colourless acid-binding salts used in accordance with this invention to impregnate the organic fibrous material include the alkali and alkaline earth metal salts of the lower alkoic monocarboxylic acids such as sodium, potassium and magnesium acetates and propionates and the carbonates and basic carbonates of those metals of Groups I and II of the Periodic Table according to Mendeleef which are available in colourless form, for example, calcium and magnesium carbonates and basic magnesium carbonate. There may also be used salts of amines with the said alkoic monocarboxylic acids, which amines do not discolour in contact with air, in particular the salts thereof with primary, secondary or tertiary alkylamines, secondary and tertiary cycloalkylamines, and secondary and tertiary saturated heterocyclic amines: examples of such amines are diethylamine, dibutylamine and piperidine. A mixture of one or more of the aforesaid alkali or alkaline earth metal salts and of an amine salt may be used: for certain purposes the use of such mixtures is particularly advantageous.

Two methods of impregnation of the organic fibrous material are available. The method of choice for any given thermoplastic polymer and the nature of the acid-binding salt or salts used will depend upon the method by which the polymer has been produced and the nature of the acid-binding salt or salts chosen. Many thermoplastic polymers which may be used are produced by aqueous emulsion polymerisation and providing the resulting emulsion is, or can be rendered, sufficiently free from oxidising agents it provides an excellent medium, after dissolving or suspending the selected acid-binding salt or salts, for directly impregnating the fibrous tissue. Alternatively, a polymer may be selected which is readily soluble in a cheap organic industrial solvent, such as industrial alcohol, and a solution prepared therein. In this solution there is then dissolved or suspended the selected acid-binding salt or salts and the resulting composition then used for impregnating the organic fibrous material. Such materials may have an overall weight of 20-70 grams per square metre, but heavier materials may be used for surfaces not having reading matter thereon, e.g. up to 100 grams per square metre.

The acid-binding agent used in the present invention serves different purposes. On the one hand it is intended to protect the document after the treatment from pollutants in the atmosphere with which it may be in contact. Even more important in the case of documents which are already a century or more old is the removal from the cellulosic tissue of acid already present therein: this has been found to be as high as 1.1% of its weight present either as free acid or the readily-dissociable ammonium sulphate. A suitable choice of the acid-binding agents used in accordance with this invention enables this to be done without wetting the cellulosic tissue. Salts such as potassium acetate, dibutylamine acetate and piperazine propionate readily permeate the tissue at temperatures of 50-100°C., and neutralise the acidity present therein. This has been proved by impregnating cellulosic tissues with pH indicators which change colour at different pH values and then noting the changes in colour which occur on and after laminating at temperatures between 50 and 100°C. If such a salt is used alone considerable care is necessary in storage and it is therefore preferred to use a mixture of a more mobile salt, such as one of the amine salts, and a less mobile salt such as magnesium acetate.

It is recommended that the impregnated organic fibrous material used should contain at least sufficient acid-binding agent to remove the above-indicated amounts of acid. If such a fibrous material is applied to each side of the document this should provide an adequate excess, but if it is intended to apply a foil or tissue to one side only, sufficient acid-binding agent should be present to remove at least twice the above amount of acid.

The less mobile acid-binding agents are used in finely divided state and require to be chosen with discretion. All material used should at least pass a 100 mesh British Standard Sieve unless used in solution to impregnate the fibrous material. Preferably the finely divided material should be a substatially inpalpable powder. In addition the material used should have a refractive index approximating to that of the thermoplastic polymeric material employed.

The preferred thermoplastic non-tacky polymer is a polyvinyl acetate, preferably of medium viscosity. A polyvinyl acetate emulsion can readily be used to impregnate an organic fibrous material. Polyvinyl acetate can readily be used in laminating operations at 80-100°C.; it readily flows into the pores of papers of all kinds at these temperatures and also adheres well to the bonded-fibre fabrics. Moreover, it is readily soluble in industrial alcohol and if delamination should be required at any time this solvent may be easily used to effect it. Copolymers of vinyl acetate containing not less than 75%, prefer-

ably at least 85%, by weight of vinyl acetate are likewise extremely useful. Preferred monomers for copolymerising with vinyl acetate are the ester monomers noted above and hydrocarbon monomers such as ethylene and propylene. In all cases in which a comonomer is used films obtained therefrom must be non-tacky at room temperature but must flow under pressure at temperatures not exceeding 120°C.

In producing a laminated product in accordance with the invention the preferred procedure is to place a sheet of a book or other document between two sheets of impregnated organic fibrous material containing acid-binding agent or agents. The whole is then compacted under pressure at a temperature below 120°C., preferably between 50 and 110°C. A photographic dry-mounting press of simple type can be used for this paper. Pressing for one minute is usually sufficient but the lower temperatures usually require longer times and may need higher pressures. The time may also require to be correlated with the rate of diffusion of a mobile acid-binding agent into the sheet being processed. The two sheets of impregnated organic fibrous material used may be like or unlike in character.

An example of an impregnated web containing two different acid-binding agents is a lens tissue of polyethylene terephthalate bonded-fibre fabric impregnated with 30 gms. per square metre of polyvinyl acetate, 0.5 gms. per square metre of magnesium or potassium acetates and 0.5 gm. per square metre of dibutylamine (as the acetate).

The following examples illustrate materials used and the process of laminating in accordance with the invention.

Example No.	Impregnated Fibrous Material				Medium used for Impregnation	Temperature °C.	Remarks
	Tissue	Polymer Thermoplastic	Acid Binding Agent	Plasticiser weight % of polymer			
1	Lens tissue	P.V.A. (m.v.)	Magnesium acetate	—	Industrial alcohol	85	
2	do	do	Sodium acetate	—	do	85	
3	do	do	Potassium acetate	—	do	85	
4	do	do	Dibutylamine acetate	—	do	85	Dry at low temperature
5	do	Ethyl cellulose	Magnesium carbonate	20% dibutyl phthalate	do	90	
6	do	P.V.A. (m.v.)	Calcium carbonate	—	do	85	
7	"Tigaweb"	do	Potassium acetate	—	do	85	
8	Regenerated cellulose bonded-fibre fabric	do	do	—	do	85	
9	Glassine	do	do	50% dibutyl phthalate	do	Room temperature	
10	Lens(1) tissue	do	do	do	do	do	
11	Lens tissue	P.V.A. (aqueous emulsion)	Calcium acetate	—	Water	90	

(1) Subsequently given thin coating of solution of a soluble nylon in anhydrous isopropyl alcohol.

P.V.A.=Polyvinyl acetate

m.v.=medium viscosity

Notes on Examples.

1. The lens tissue used was fabricated from long hemp fibre cellulose and weighed 9 gms. per square metre.
2. "Tigaweb" is a bonded-fibre fabric made from polyethylene terephthalate fibres: it is about 0.07 mm. thick.
3. In all cases the thermoplastic polymer was applied to the tissue in such quantities as to deposit 10-40 gms. per square metre.
4. The polyvinyl acetate aqueous emulsion used in Example 11 was "Emultex" K 505 (Registered Trade Mark).
5. The dibutylamine acetate used in Example 4 was deposited in an amount of 2 gms. per square metre.
6. The magnesium carbonate used was of pharmaceutical grade: the calcium carbonate was precipitated chalk.
7. The product of Example 4 should be dried at room temperature so as to avoid loss of amine.

The dry weight of the impregnated tissues before laminating lay substantially between 20 and 50 grams per square metre in all cases. Using the conditions set forth in the table, pages from books printed more than 250 years ago have been satisfactorily strengthened and deacidified by laminating at temperatures which did not exceed 90°C. No additional discoloration was observed to occur under these conditions whereas when plasticised cellulose acetate (plasticiser: dibutyl phthalate) is used at 170-180°C. additional discoloration occurs. All the pages were simultaneously strengthened and deacidified (the deacidification was most rapid with dibutylamine acetate). The resulting laminates were quite flexible.

WHAT I CLAIM IS:—

1. A process for the preservation of a document having as its basis an opaque fibrous cellulosic web which comprises applying to at least one surface of said document a translucent thin colourless flexible web of organic fibrous material impregnated with a mixture of (a) a substantially colourless flexible inert film-forming thermoplastic non-tacky material which is resistant to oxidation and degradation in air at room temperatures and which will flow under pressure at temperatures not exceeding 120°C., and (b) at least one colourless acid-binding salt present in an amount at least sufficient to neutralise the acidity present in said opaque fibrous cellulosic web, and compacting the resulting laminate under pressure at a temperature not exceeding 120°C. until said non-tacky material has adhered to the surface of said opaque fibrous cellulosic web.

2. A process according to claim 1 in which one acid-binding salt is a salt of an amine which does not discolour in contact with air.

3. A process according to claim 2 in which, in addition to a salt of said amine, a less mobile acid-binding salt is also present.

4. A process according to any of the preceding claims in which the flexible inert film-forming thermoplastics material is a non-tacky polymer of a mono-ethylenically unsaturated ester of a monocarboxylic acid, which polymer contains only carbon, hydrogen and oxygen atoms.

5. A process according to claim 4 in which the film-forming material is a polyvinyl acetate or a copolymer of vinyl acetate containing not less than 75% by weight of vinyl acetate.

6. A process according to any of the preceding claims in which the fibrous material is a translucent tissue paper or a bonded-fibre fabric.

7. A process according to claim 6 in which the bonded-fibre fabric is a polyethylene terephthalate bonded-fibre fabric.

8. A process for the preservation of a document according to claim 1 and substantially as hereinbefore described.

9. Documents preserved by the process of any of the preceding claims.

10. A translucent thin colourless flexible web of organic fibrous material impregnated with a mixture of (a) a substantially colourless flexible inert film-forming thermoplastic non-tacky material which is resistant to oxidation and degradation in air at room temperatures and which will flow under pressure at temperatures not exceeding 120°C. and (b) at least one colourless acid-binding salt.

11. Material according to claim 10 in which one acid-binding salt is a salt of an amine which does not discolour in contact with air.

12. Material according to claim 11 in which, in addition to said amine salt, a less mobile acid-bnding salt is also present.

13. Material according to any of claims 10 to 12, in which the flexible inert film-forming thermoplastic material is a non-tacky polymer of a monoethylenically unsaturated ester of a monocarboxylic acid, which polymer contains only carbon, hydrogen and oxygen atoms.

14. Material according to claim 13 in which the thermoplastic material is a polyvinyl acetate or a copolymer of vinyl acetate containing not less than 75% by weight of vinyl acetate.

15. Material according to any of claims 10 to 14 in which the fibrous material is a translucent tissue paper or a bonded-fibre fabric.

16. Material according to claim 15 in which the bonded-fibre fabric is a polyethylene terephthalate bonded-fibre fabric.

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